

Ultrafast structural dynamics of solvated organometallic complexes and prospects for studying coherent bi-molecular reactions

*Workshop on Evolution and Control of Complexity, ANL
October 2010*

C. Rose-Petrucci

www.rosepetruck.chem.brown.edu

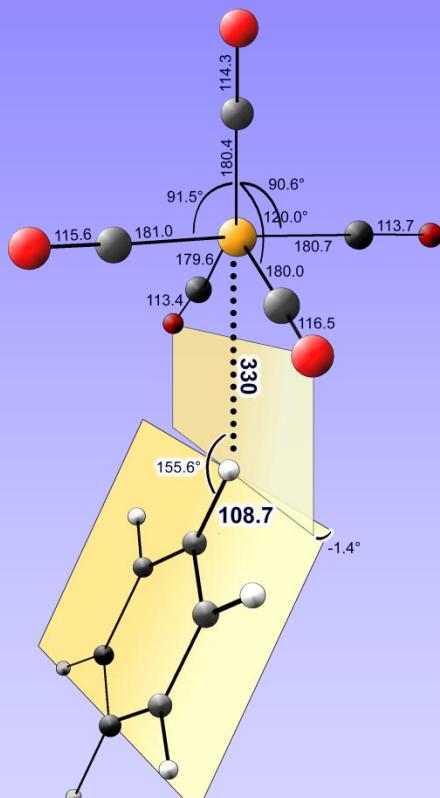


Goals

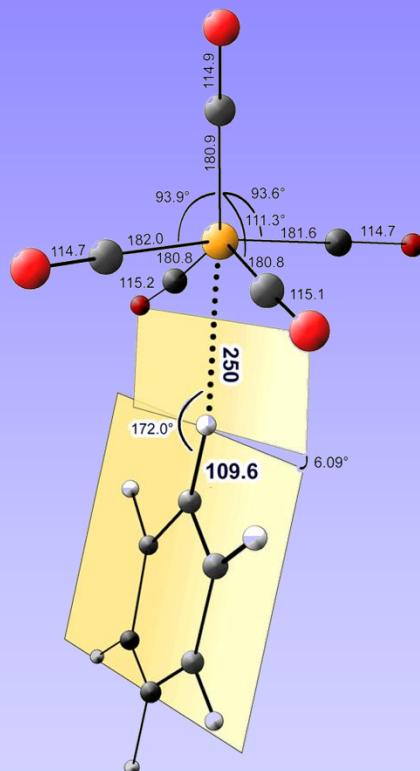
- Carry out bi-molecular reactions in solution before the onset of decoherence;
- Important because such processes may permit the coherence transfer from reactants to product molecules;
- Diffusive reactant encounter needs to be avoided;
- This might enable coherent control of reactions along the entire reaction coordinate;
- A possible experimental route: “Preassembly of reactants”
- Example system: Solvated $\text{Fe}(\text{CO})_5$



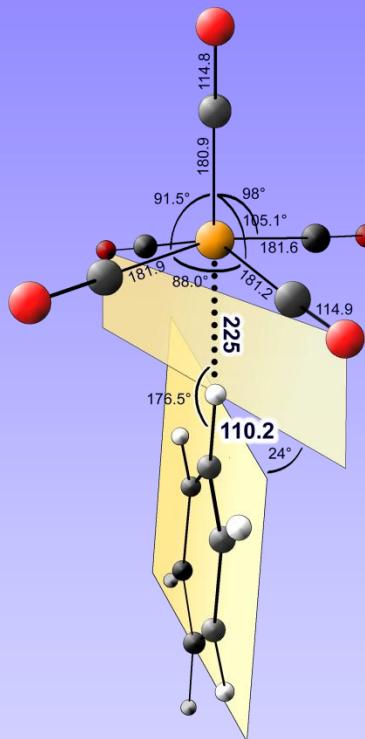
IPC-Bz structures at various solute-solvent distances



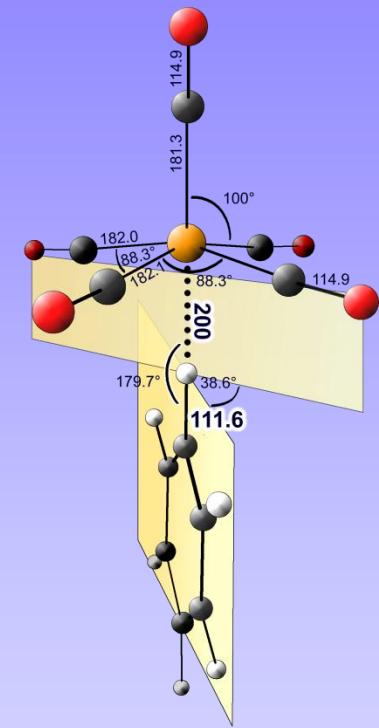
1 (IPC: $\sim D_{3h}$)



2 (IPC: C_{2v})



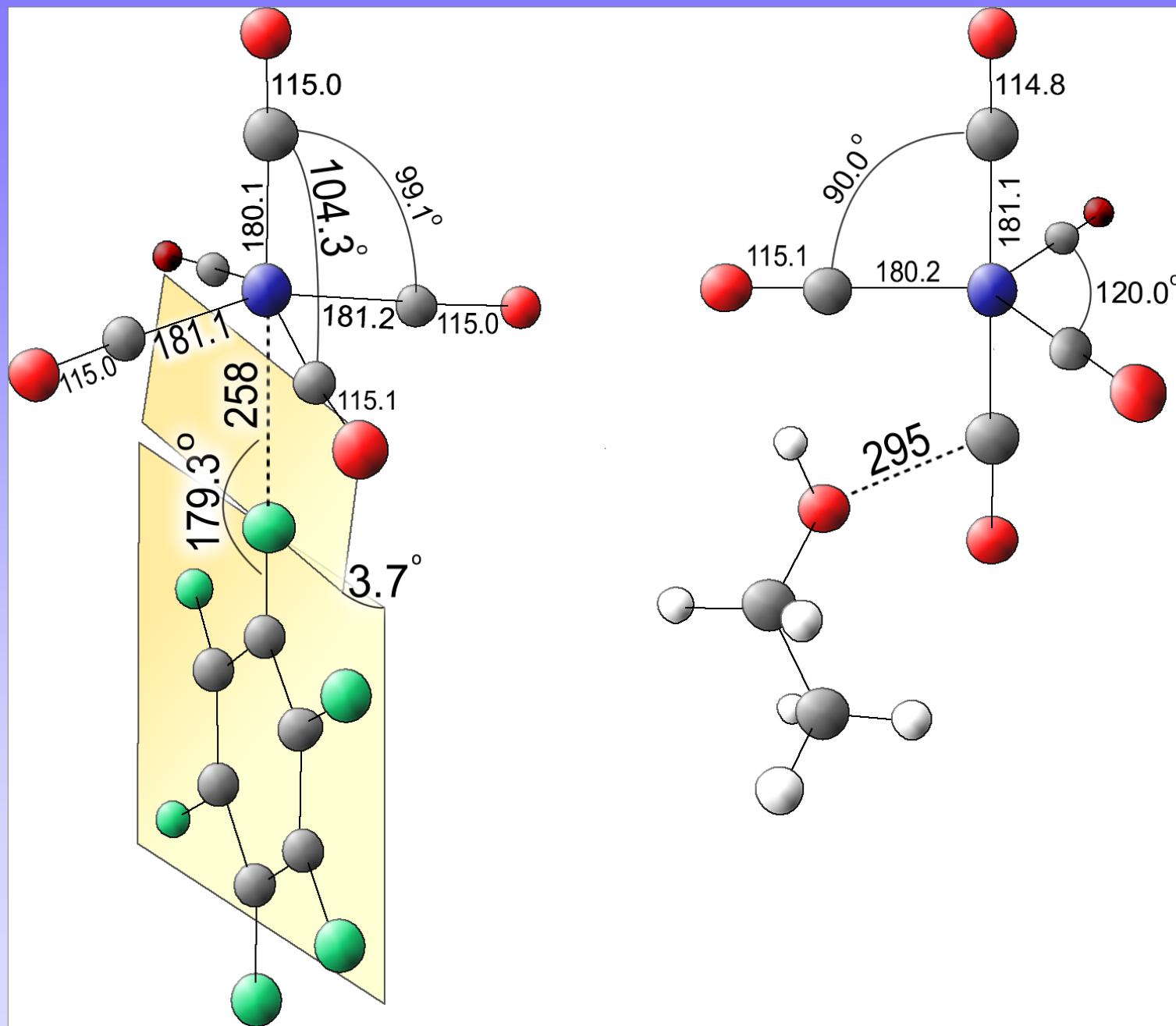
3 (IPC: C_{2v})



4 (IPC: $\sim C_{4v}$)

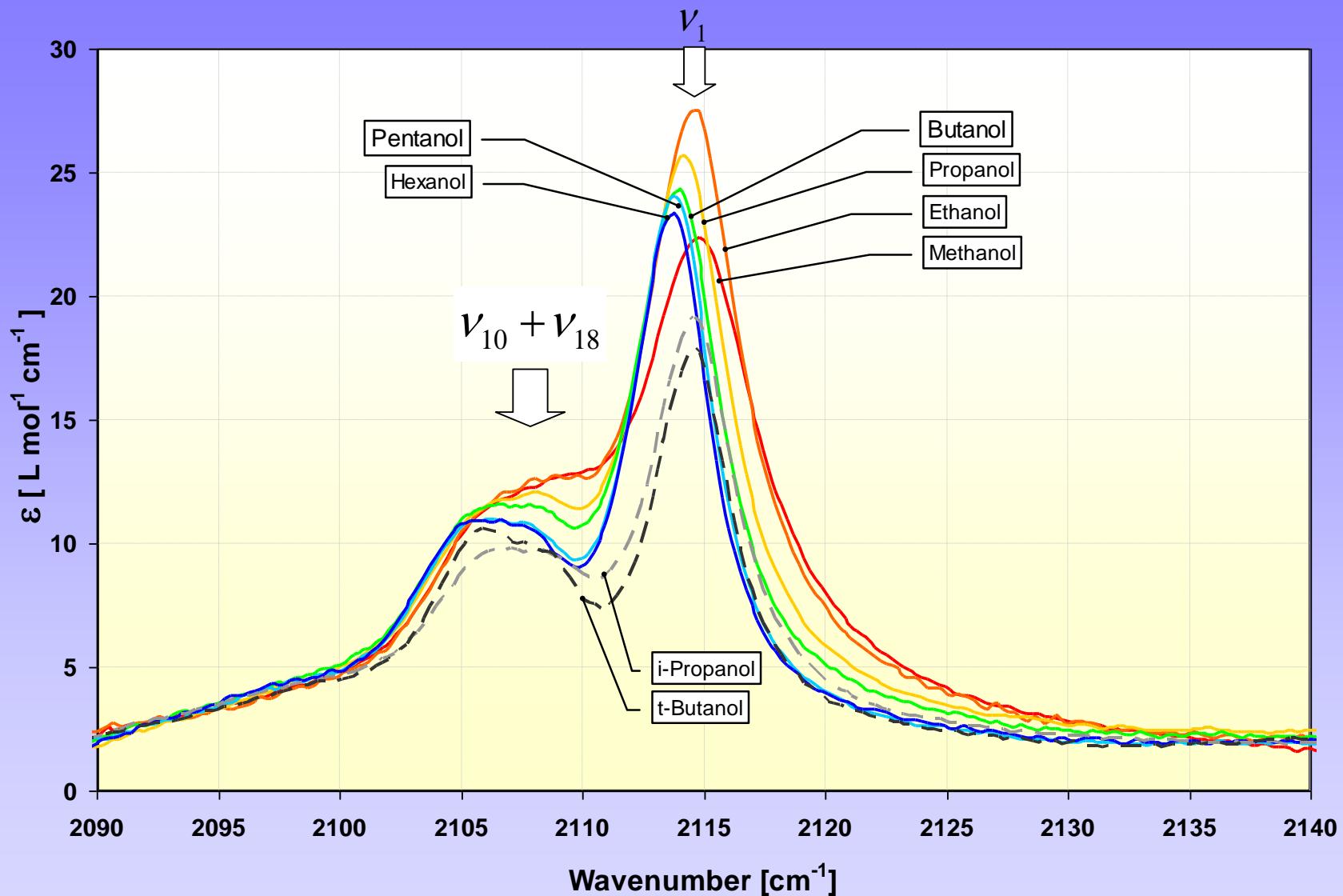


IPC···Solvent equilibrium structures





ν_1 -IR absorption spectra of IPC in a





Equilibrium thermodynamics data for solvated Fe(CO)₅

Solvent	ΔS [J / K mol]	ΔH [kJ / mol]	ΔG at 25 °C [kJ/mol]	Relative populations			IPC-Solvent distances [pm]		
	IPC (D _{3h})	IPC-solvent	XAFS data	DFT-FTIR data					
Methanol	-60 ± 22	-19 ± 8	-1 ± 1.4	38% ± 14%	62% ± 14%	R (Fe-OH)*	not measured	358 ± 28	
Ethanol	-91 ± 7	-32 ± 2	-4.47 ± 0.03	13.3% ± 0%	86.7% ± 0%	R (Fe-OH)*	not measured	356 ± 33	
Isopropanol	-80 ± 8	-25 ± 3	-0.8 ± 0.2	41% ± 2%	59% ± 2%	R (Fe-OH)*	not measured	350 ± 10	
Butanol	-42 ± 8	-14 ± 3	-1 ± 1	41% ± 10%	59% ± 10%	R (Fe-OH)*	not measured	340 ± 28	
Hexanol	-105 ± 31	-29 ± 11	3 ± 2.3	75% ± 17%	25% ± 17%	R (Fe-OH)*	not measured	375 ± 10	
Cyclohexane				100%	0%				
Bz	-47 ± 9	-15 ± 4	-1 ± 1.2	38% ± 11%	62% ± 11%	R (Fe-H)	247 ± 12		254 ^b
FBz ^a			-3 ± 0.7	28% ± 5%	72% ± 5%	R (Fe-H)	246 ± 12		248 ^b
PFBz	-35 ± 8	-15 ± 3	-4 ± 0.5	11% ± 3%	89% ± 3%	R (Fe-H)	245 ± 13		236 ^b
HFBz	-41 ± 13	-15 ± 7	-3 ± 2.8	23% ± 20%	77% ± 20%	R (Fe-F)	258 ± 2		

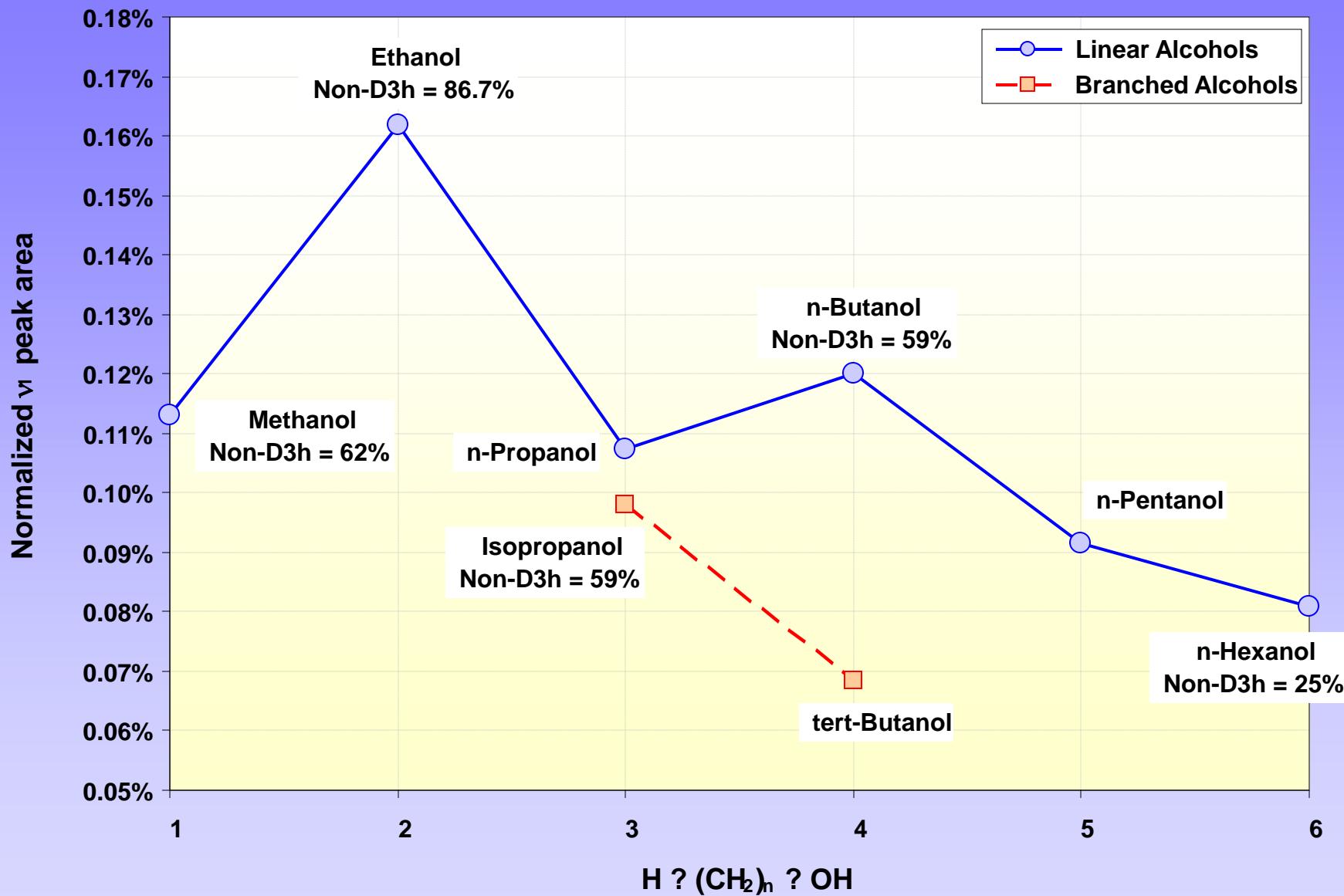
^a ΔG was obtained by using the FTIR results scaled by the DFT calculated absorption intensities for IPC···FBz at room temperature. Error is estimated.

^b During the data analysis Fe-H and Fe-F interactions were not distinguished.

All uncertainties denote 95%-confidence intervals.



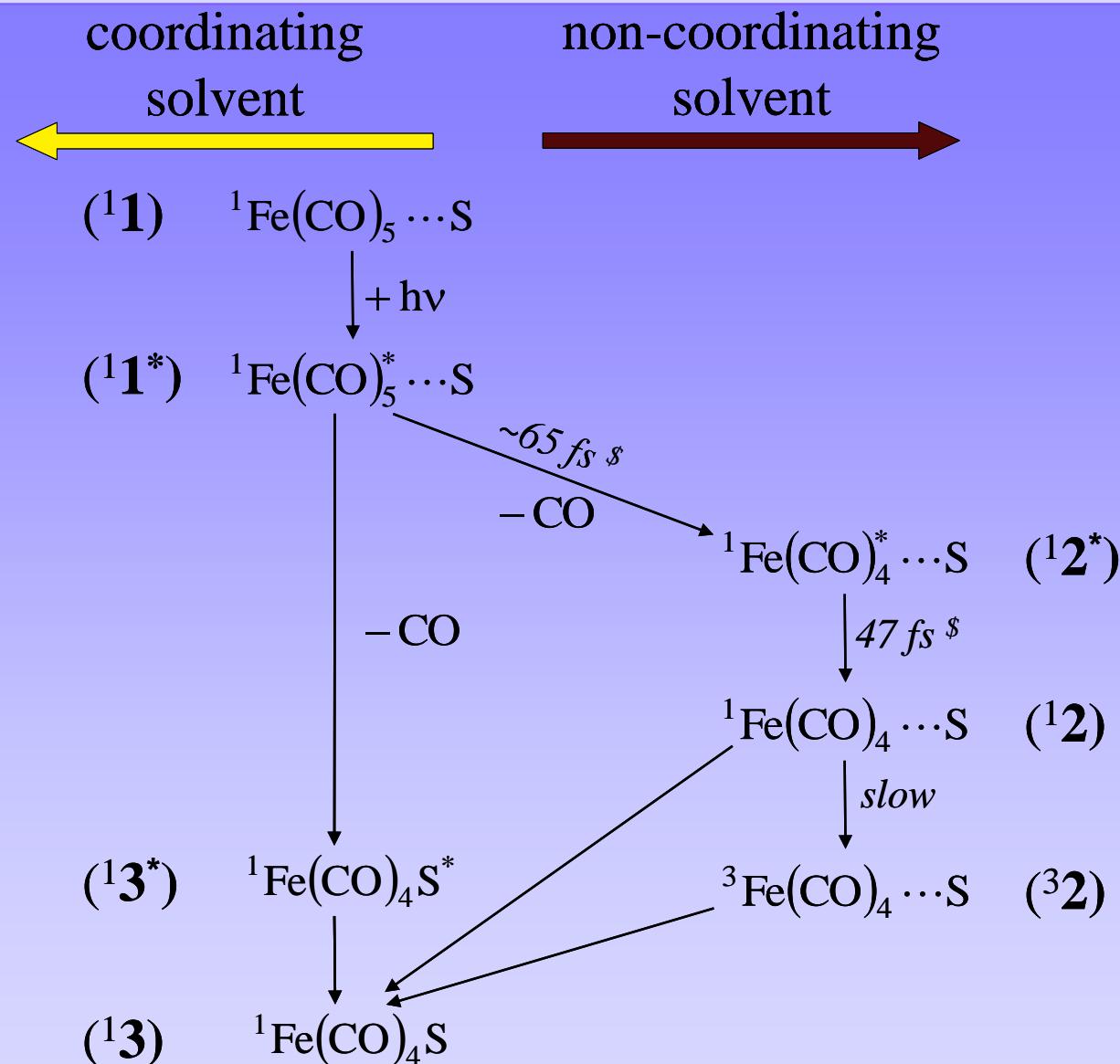
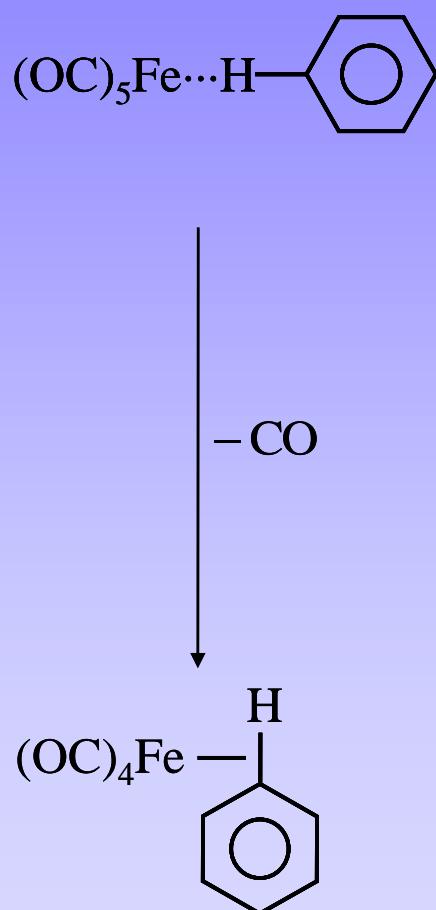
IPC-alcohol complex population at room temperature





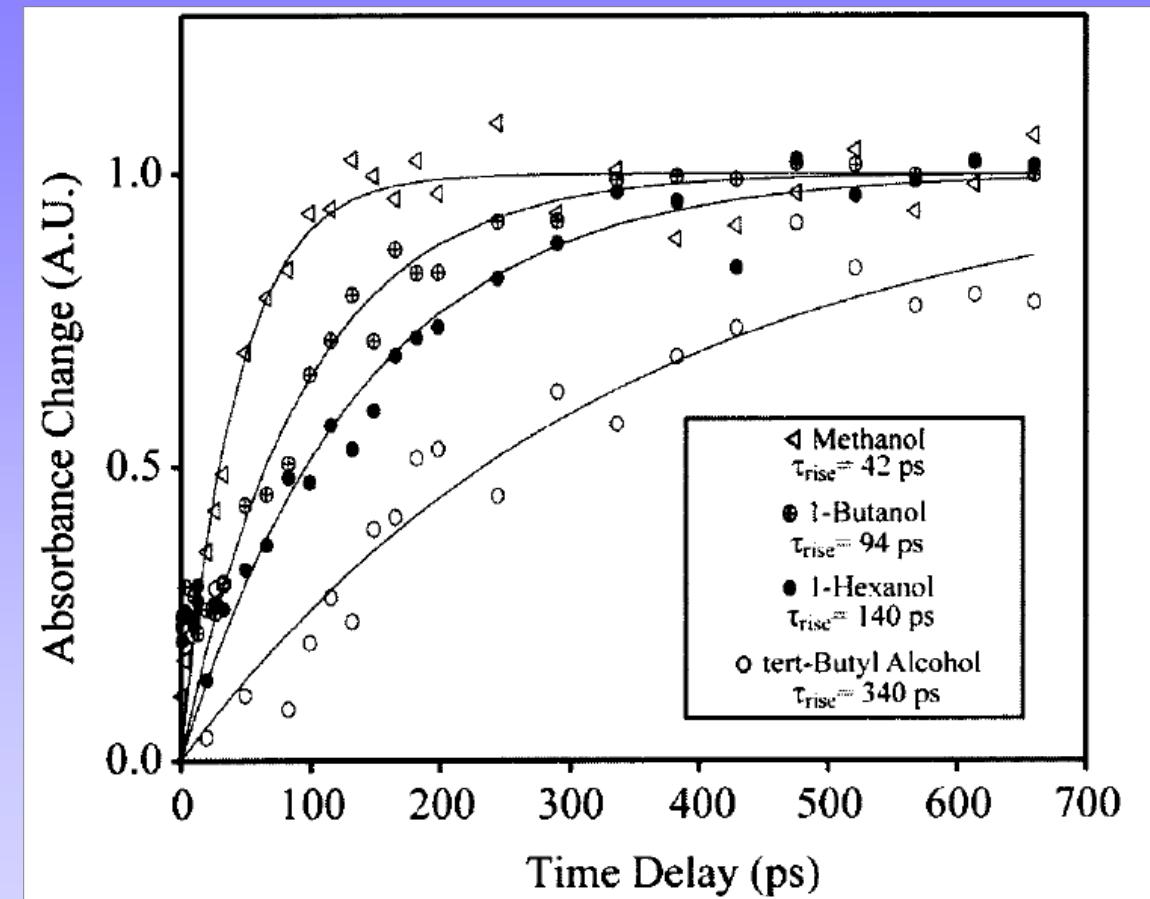
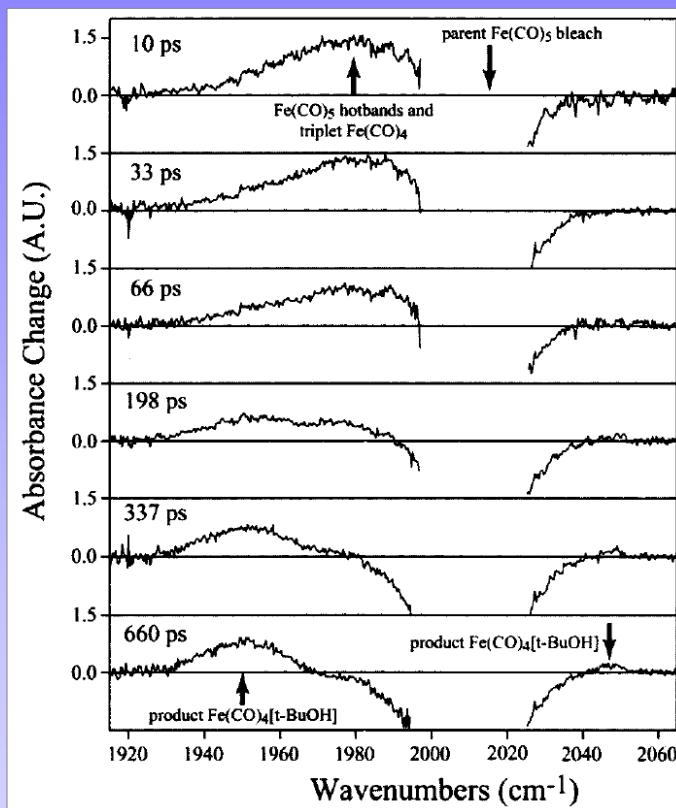
Possible IPC...Solvent reaction mechanisms

Example:



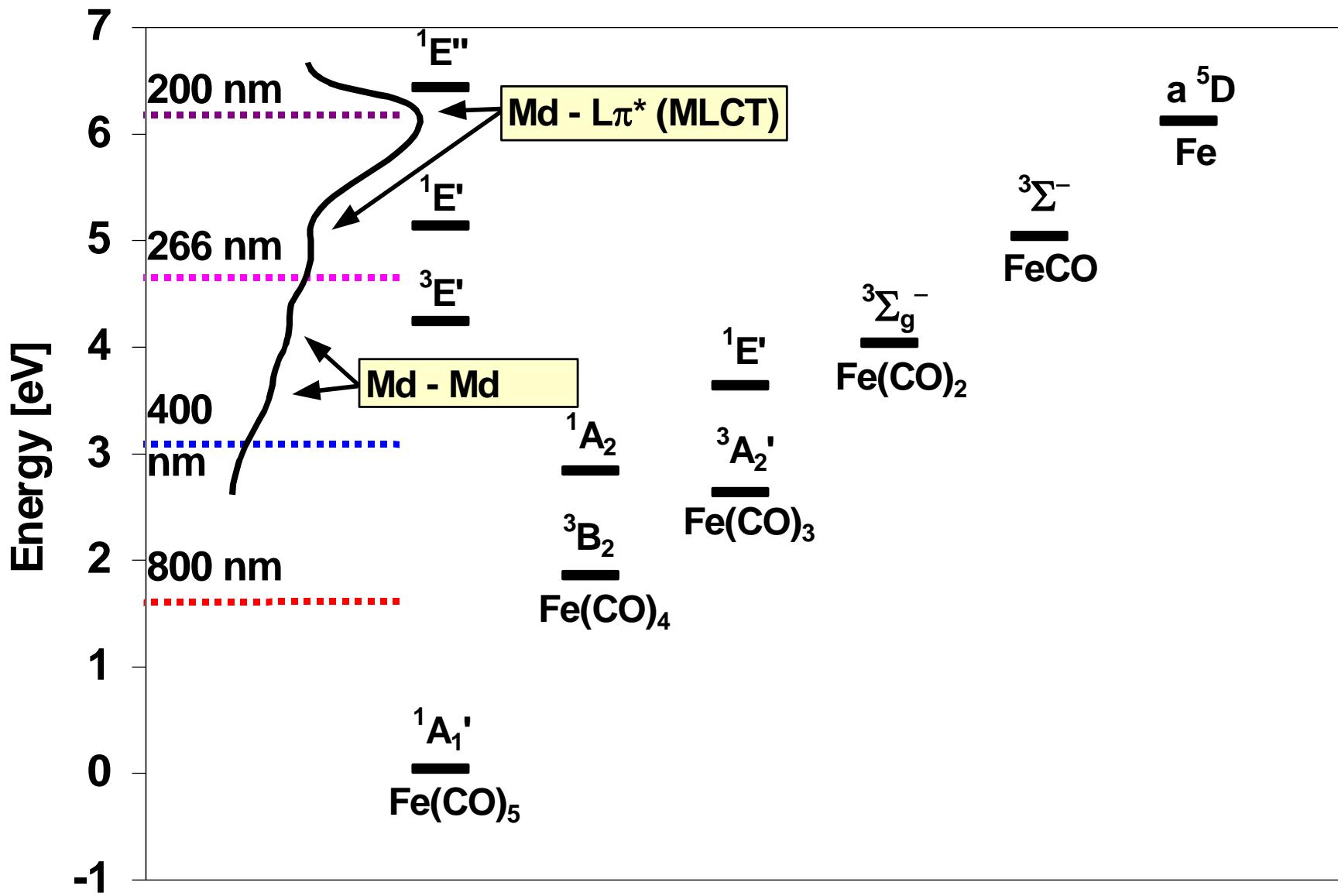


Transient IR absorption measurements of $\text{Fe}(\text{CO})_5$ in alcohols



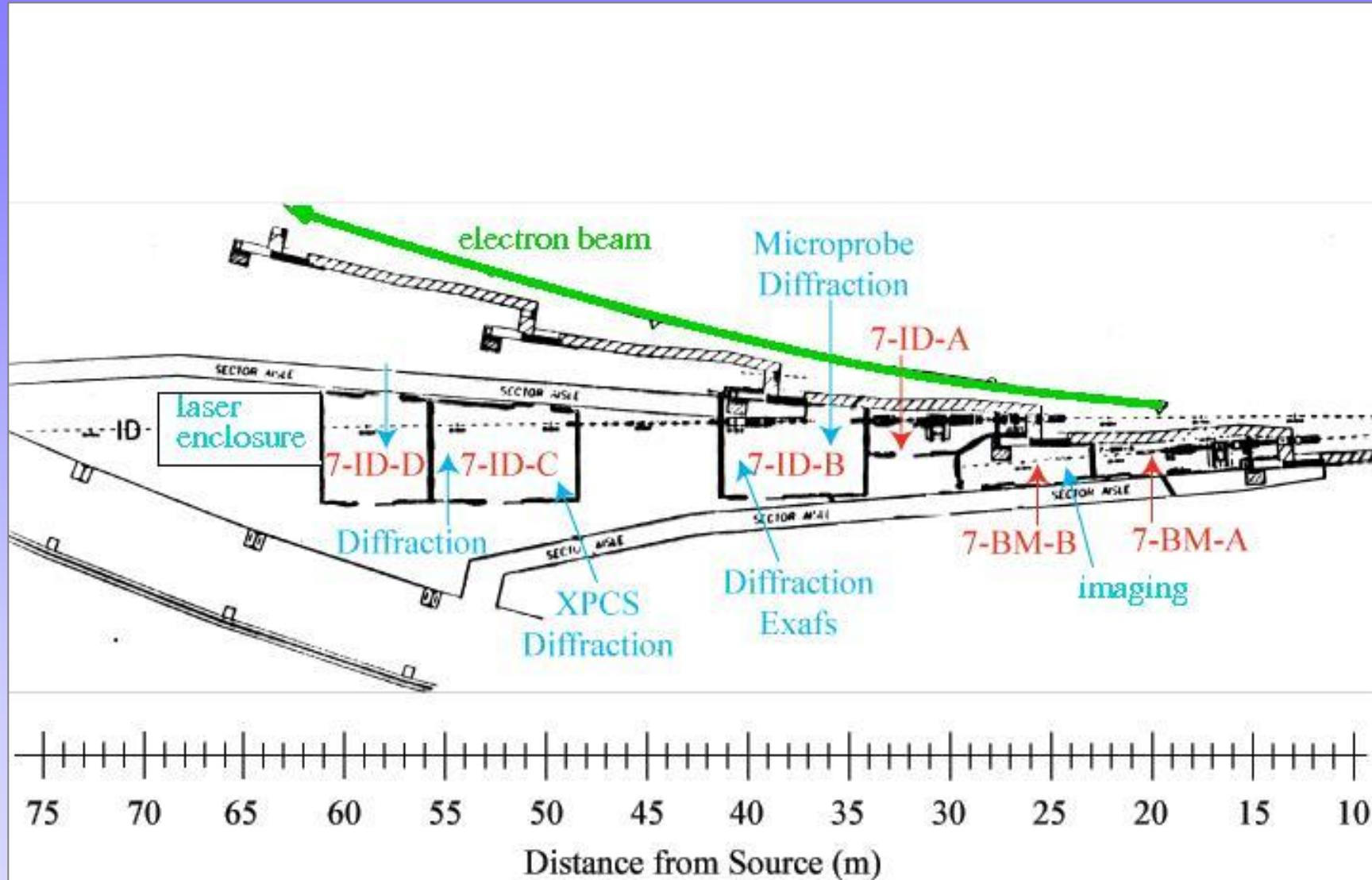


Energy levels of $\text{Fe}(\text{CO})_5$ and its photo products



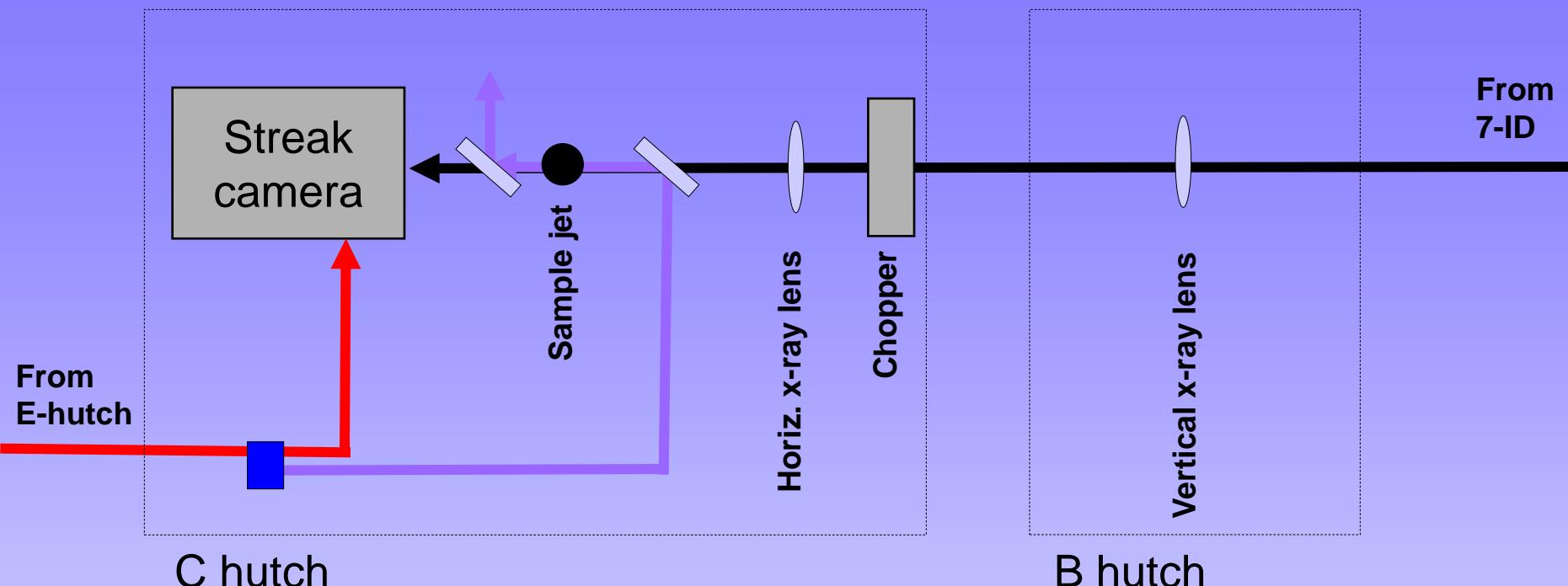


APS sector 7 layout, experiments are done at 7-ID-C





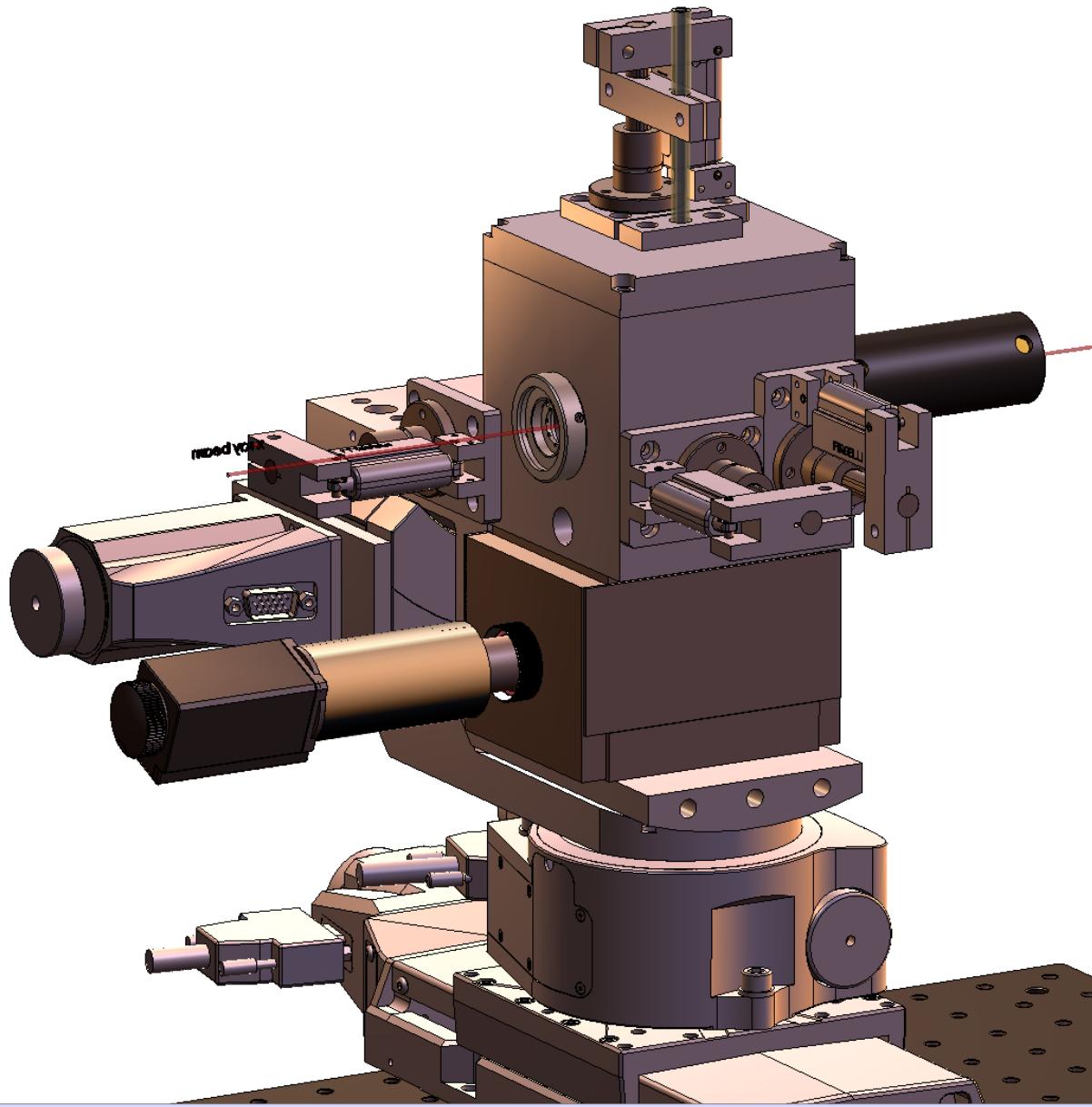
APS 7ID-C: Experimental design



	Nov. 2009	Spring 2010
X-ray spot size, horizontal	50 µm	10 µm
X-ray spot size, vertical	10 µm	10 µm
Experiment repetition rate	1 kHz	5 kHz
400-nm pump power	450 mW	1 W
Detected x-ray flux	2000 ph/s	2e5 ph/s
Data aq. time for each energy	0:41:03	0:00:25

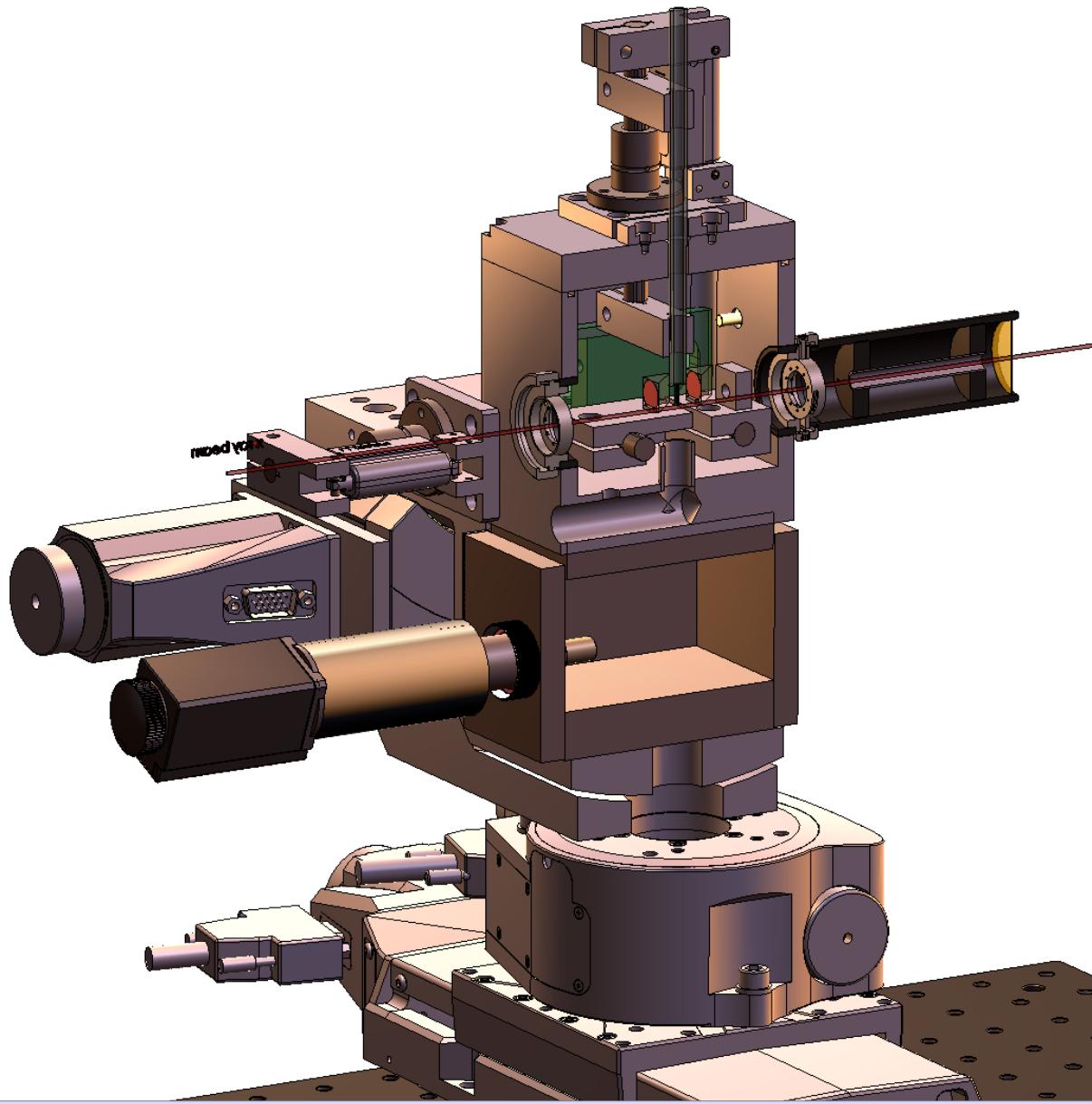


APS 7ID-C: Liquid beam apparatus



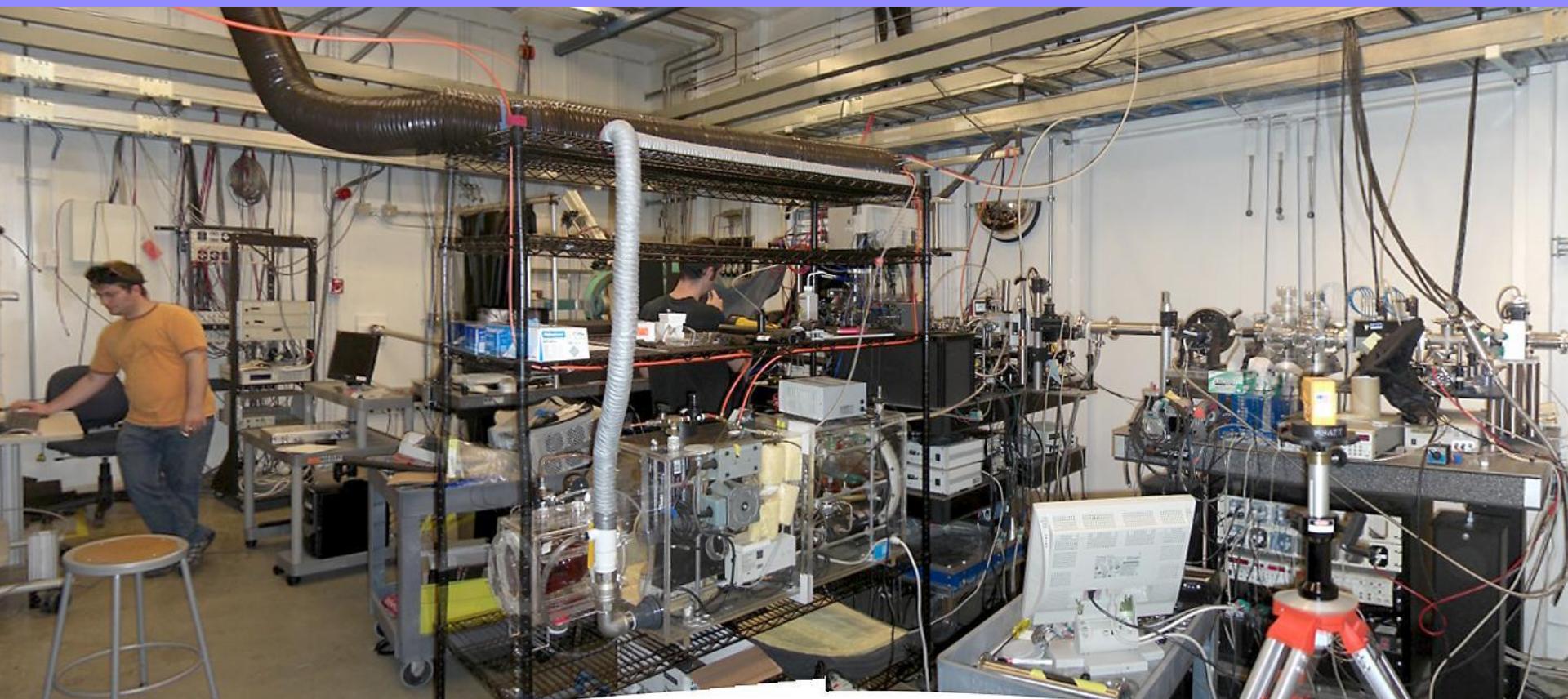


APS 7ID-C: Liquid beam apparatus, cut-away



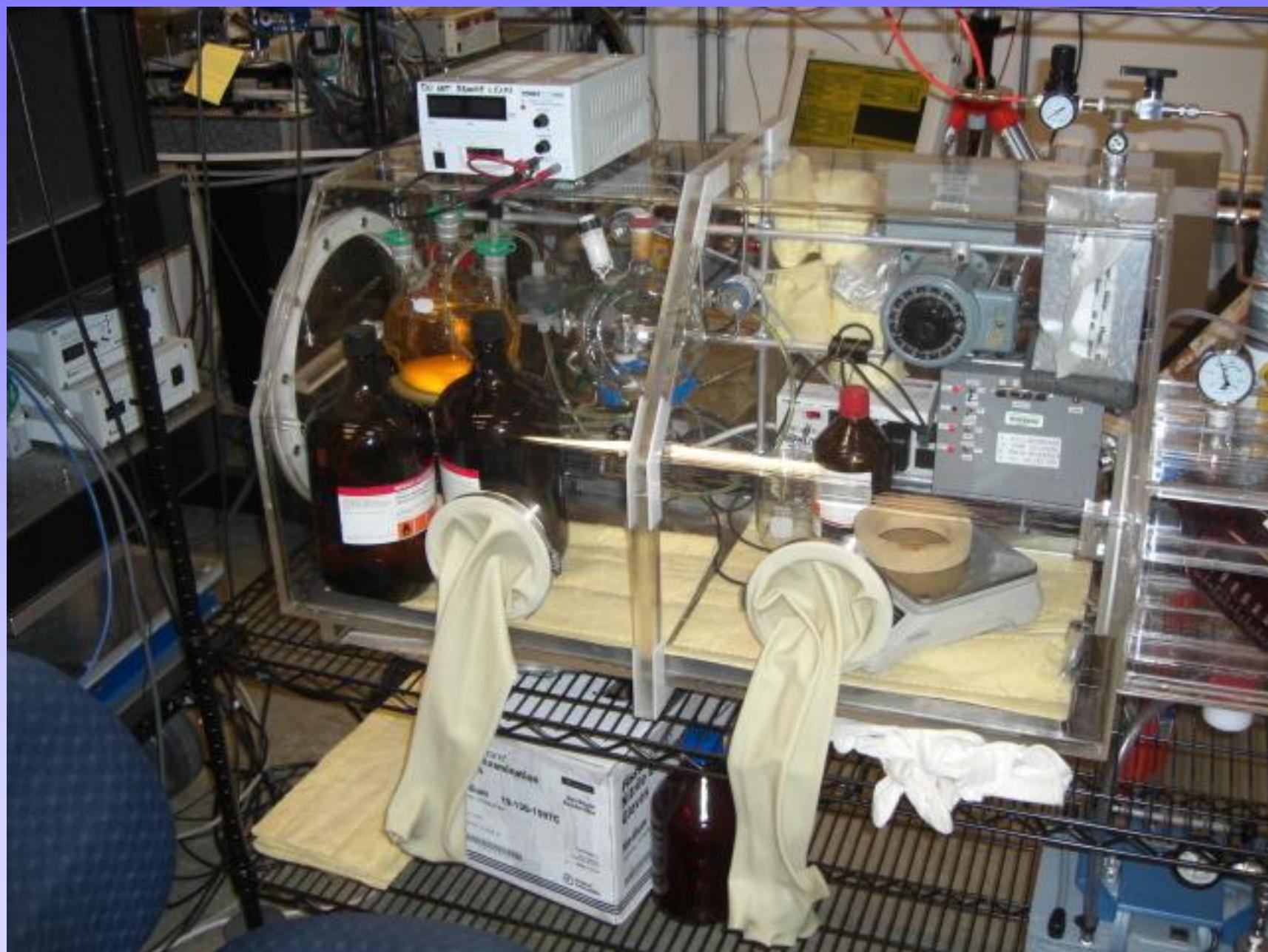


APS 7ID-C



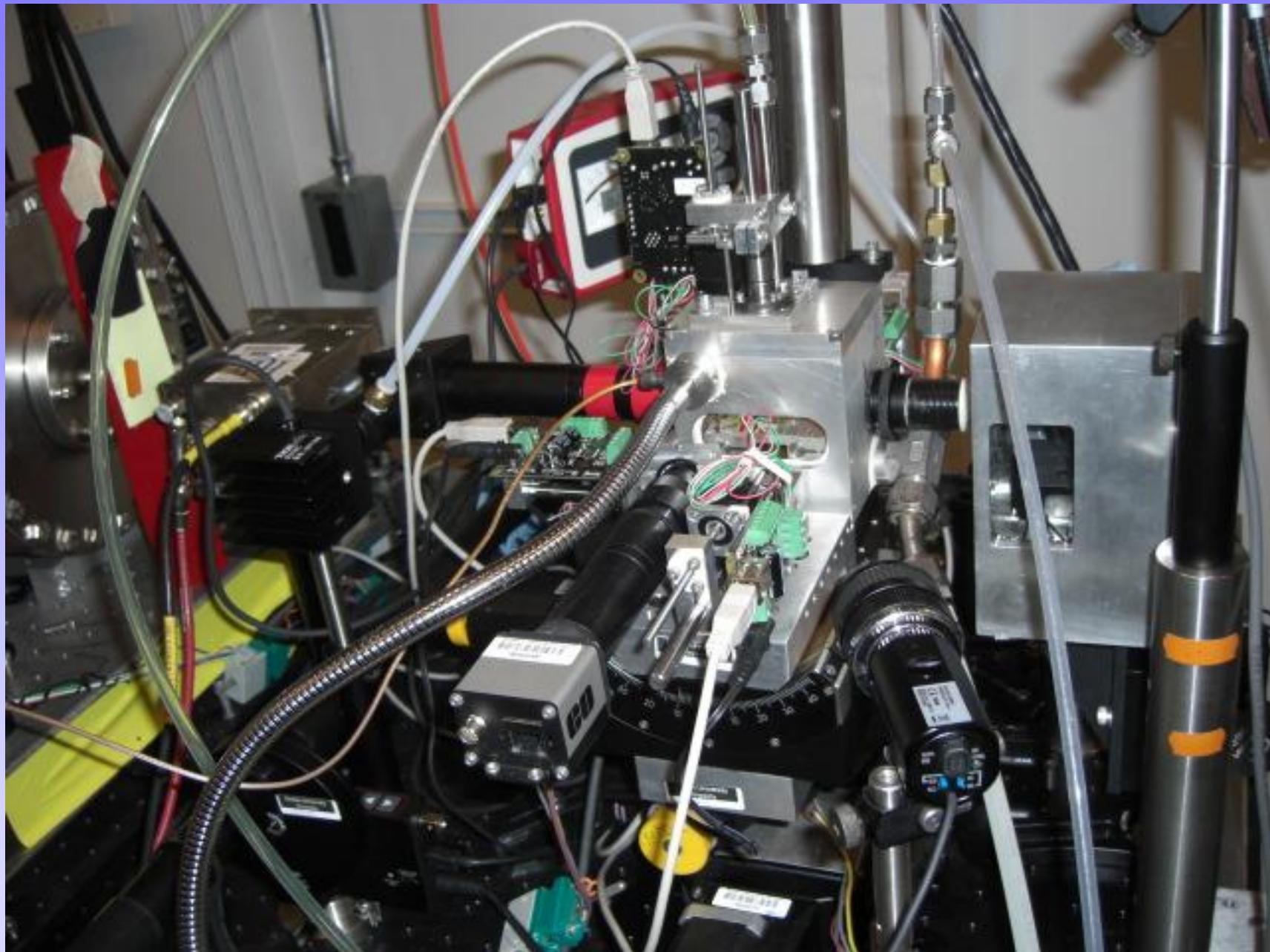


APS 7ID-C: Liquid beam apparatus and streak camera



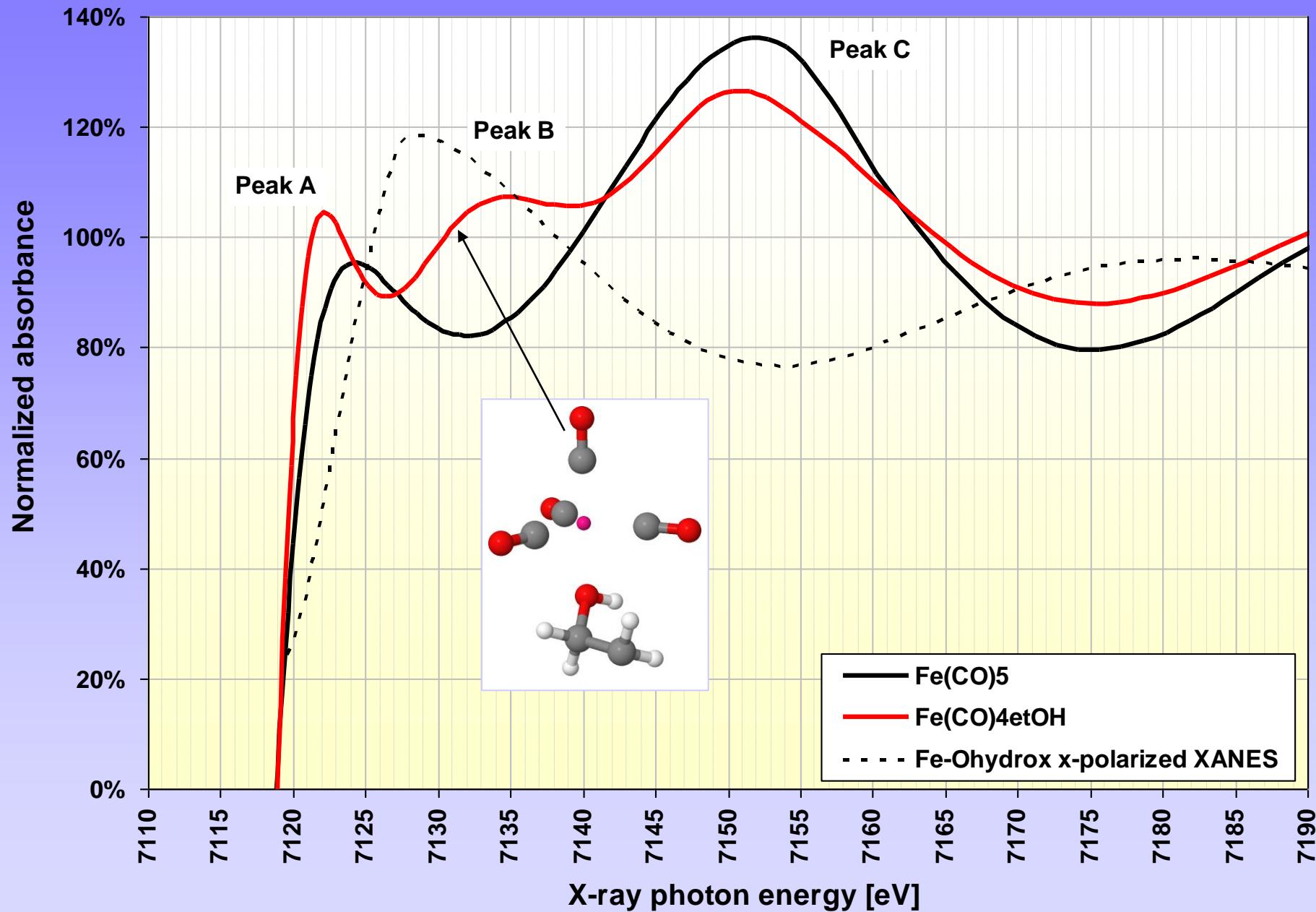


APS 7ID-C: Liquid beam apparatus and streak camera



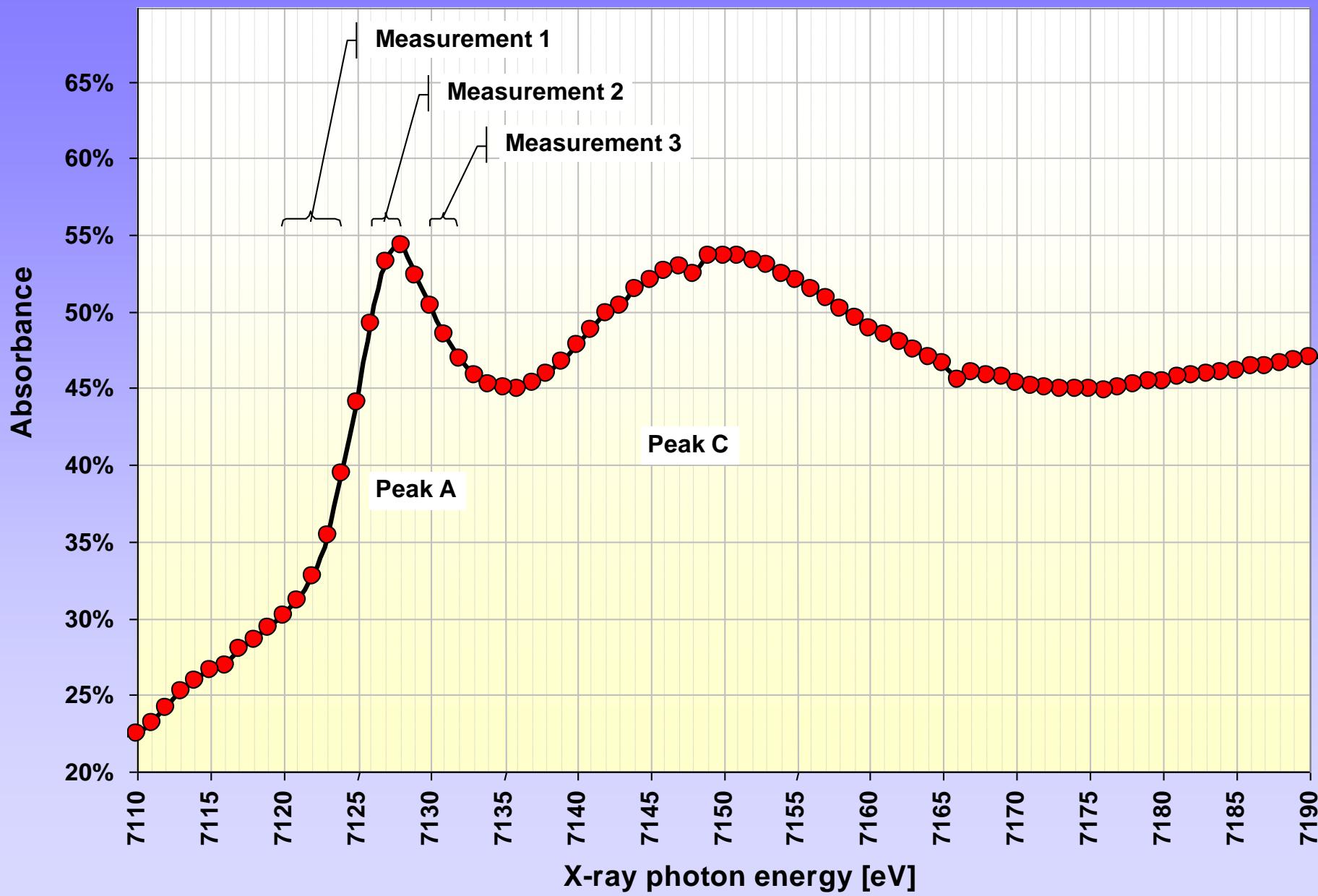


XANES of $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{etOH}$



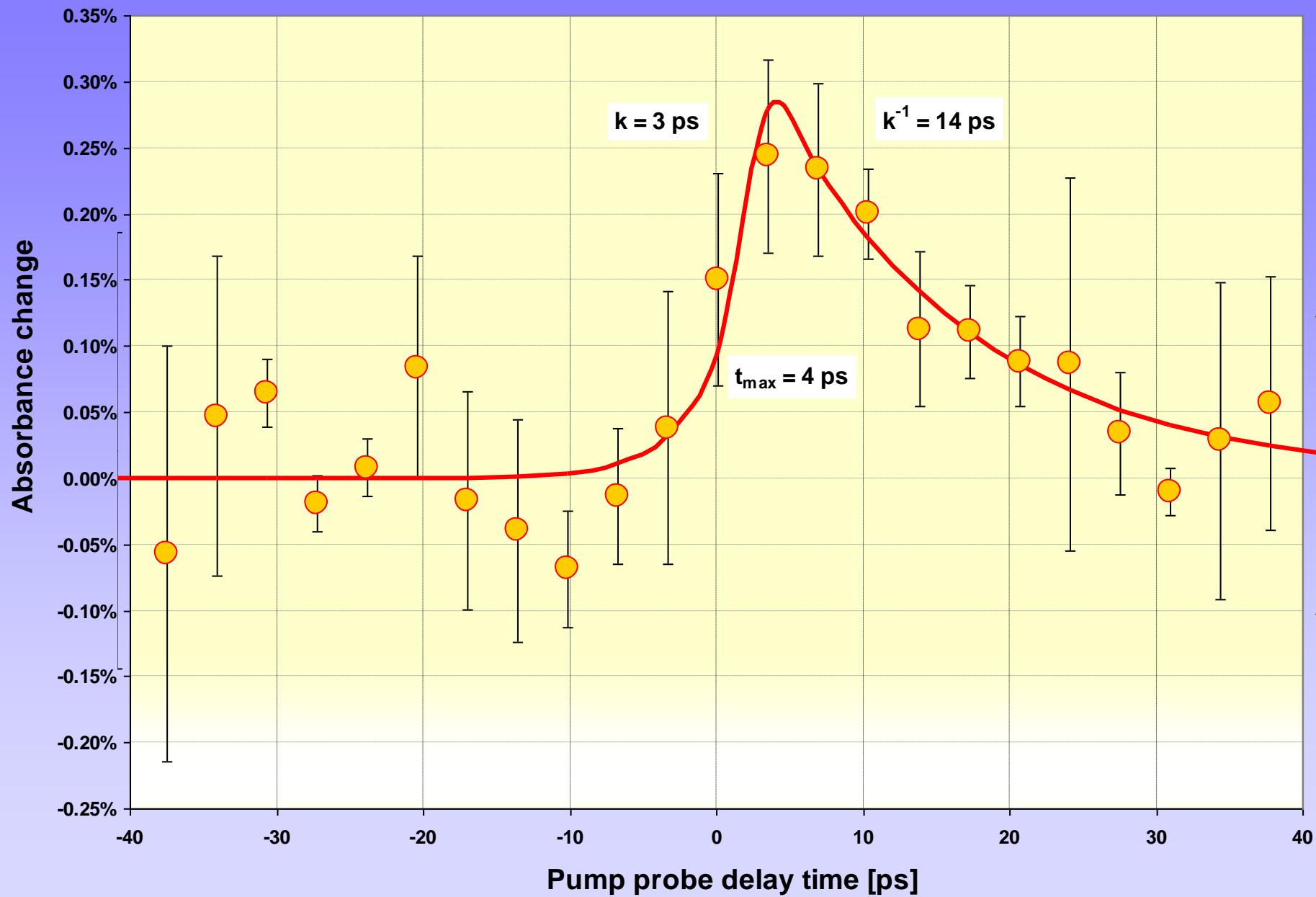


XANES of $\text{Fe}(\text{CO})_5$



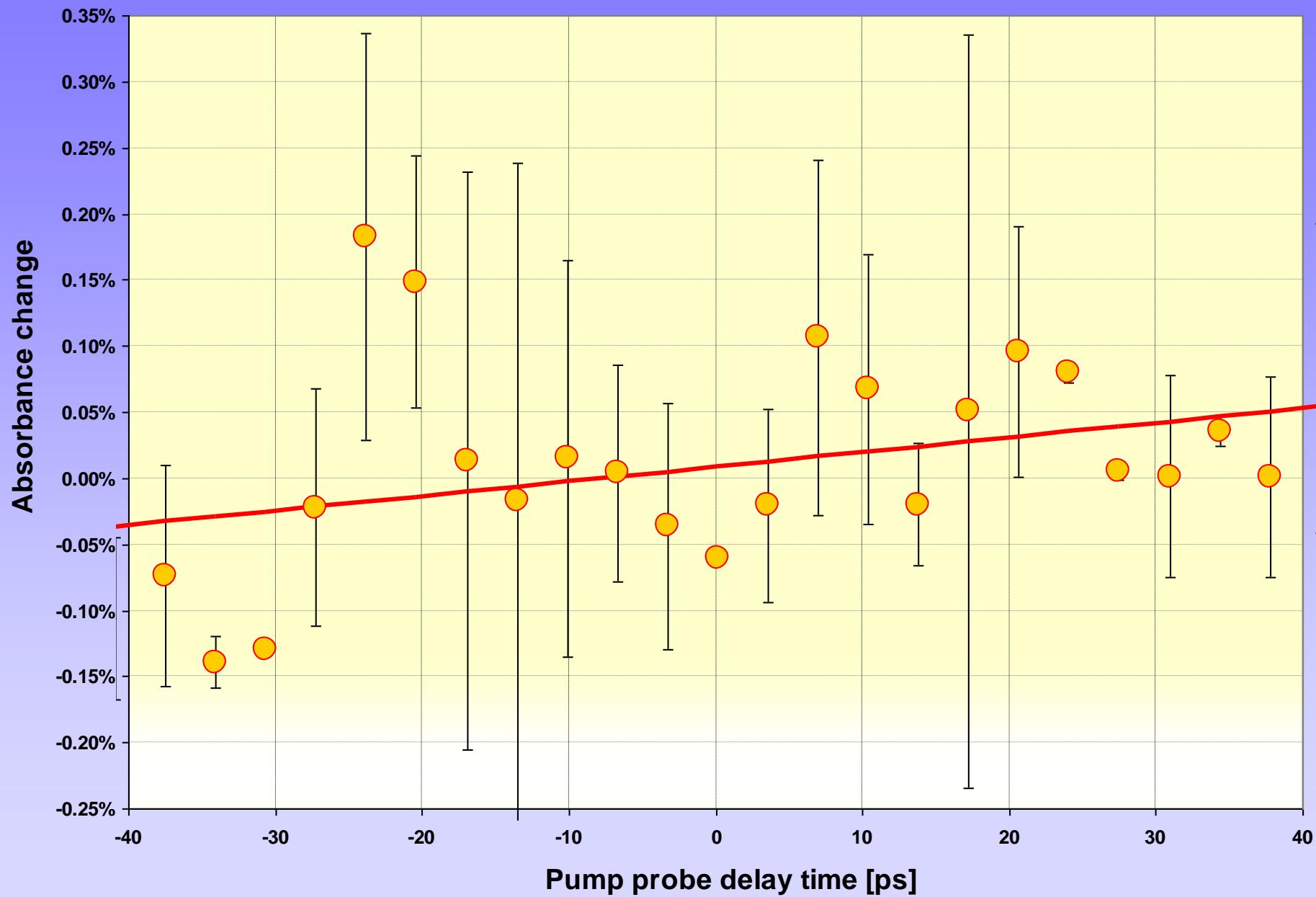


APS 7ID-C: Pump-probe signal at 7120eV – 7124eV, 95% confidence intervals shown



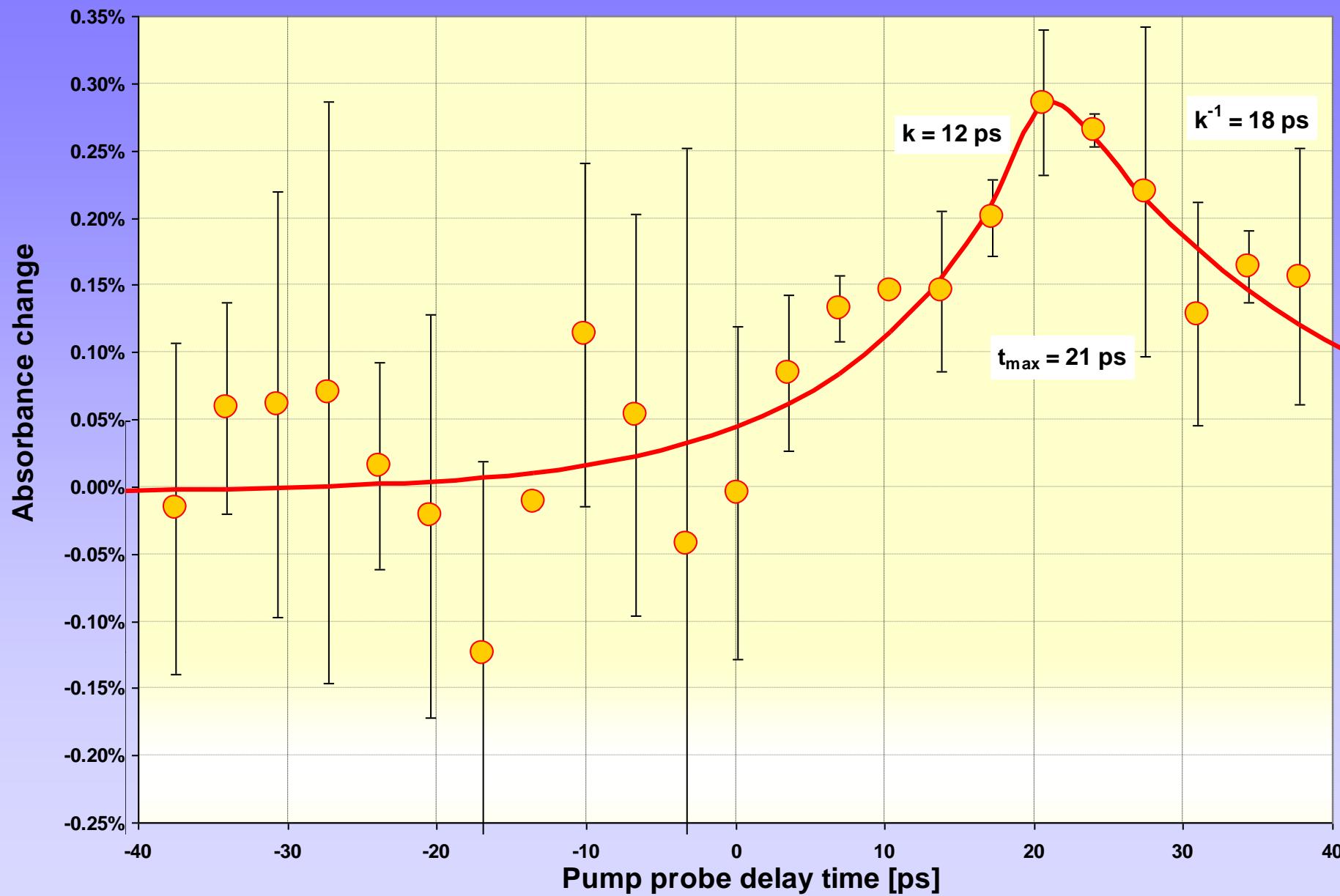


APS 7ID-C: Pump-probe signal at 7126eV – 7128eV, 95% confidence intervals shown



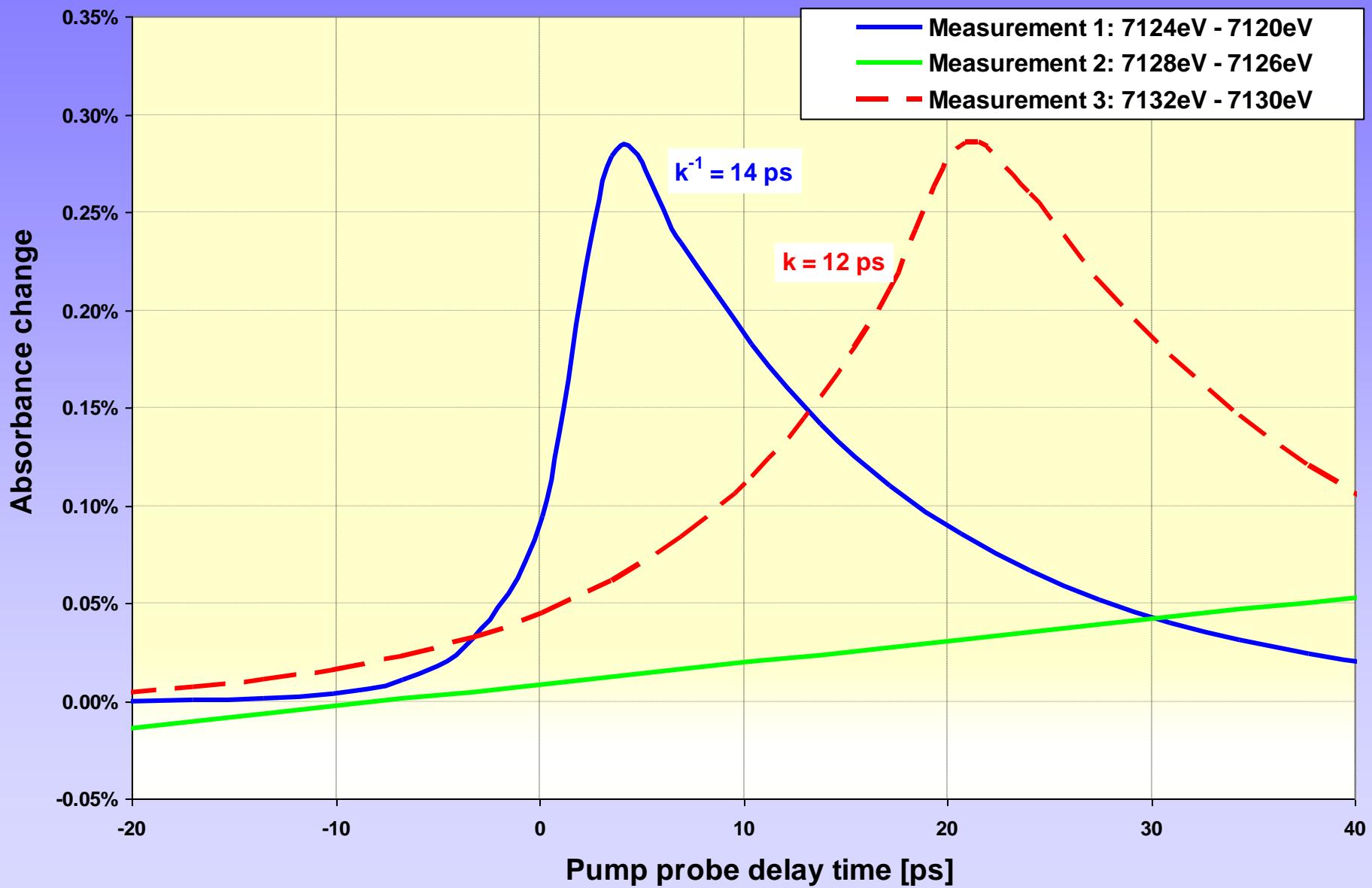


APS 7ID-C: Pump-probe signal at 7130eV – 7132eV, 95% confidence intervals shown



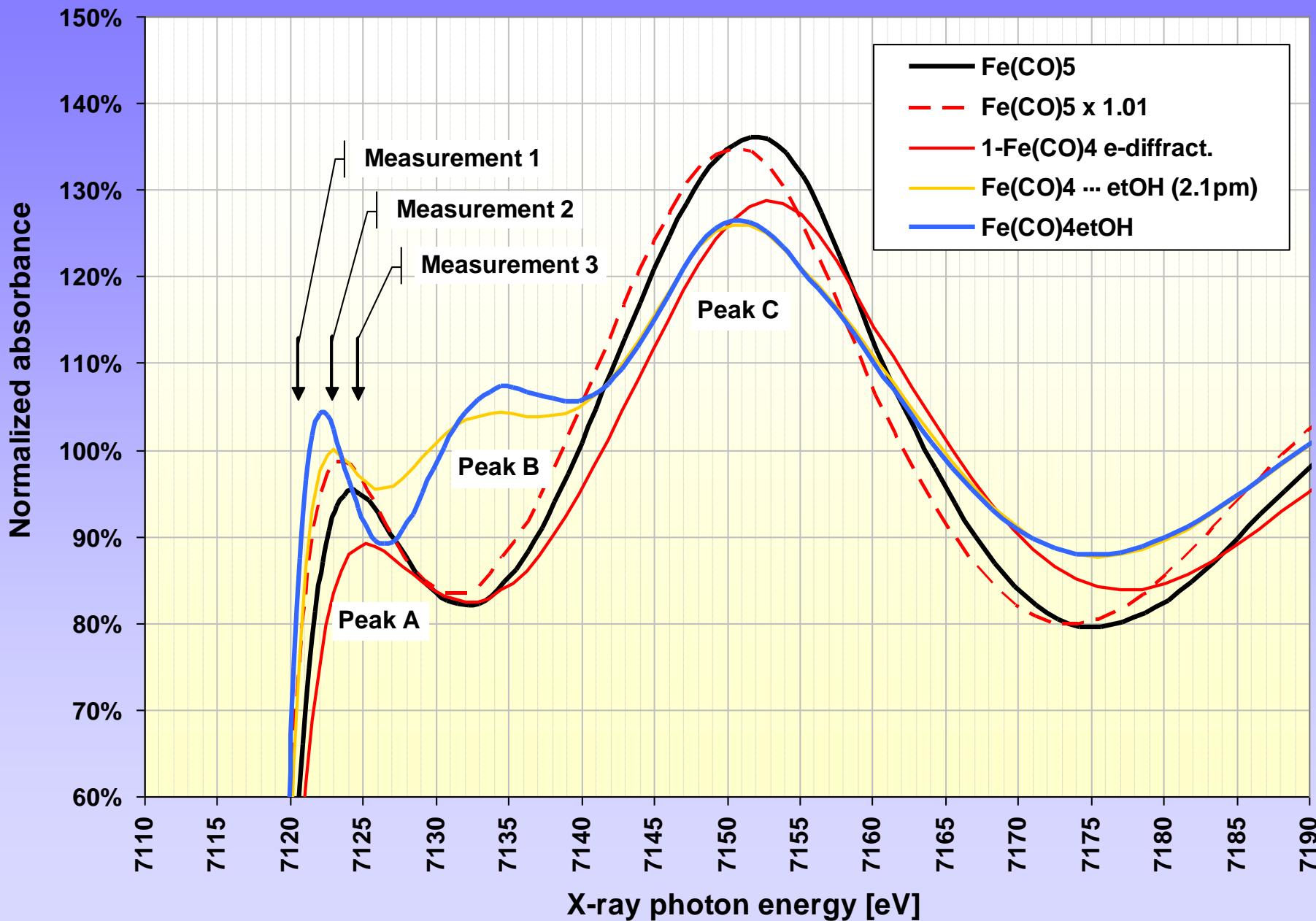


Measured rate





Theoretical XANES spectra for ligand substitution and dissociation





Summary

- **Fe(CO)₅ is saturated but sterically uncrowded.**
 - ➡ **Fe(CO)₅...Solvent pre-assembly**
 - ➡ **Reaction not diffusion limited for a large population fraction**
 - Mechanistic consequence: Concerted ligand substitution possible
 - ➡ **Coherence may transfer from reactants to products**
- **Solvation structure of penta-coordinated complexes:**
- **3-ps XANES measurements with streak camera at 7ID-C suggest ligand substitution that is not diffusion limited**
- **Higher temporal resolution needed**



Acknowledgments

X-ray imaging and ultrafast dynamics

Brian Ahr

Prof. Chris Laperle, *Providence College*

Yanan Liu

Xiaodi Li

Dr. Bernhard Adams, *Argonne NL*

Dr. Matthieu Chollet, *Argonne NL*

Carbon Capture and Sequestration

Brian Ahr

Alexander Linkin

David Herlihy

James Bickford, Mike Feng,

The Charles Stark Draper Laboratory, Inc.

Kim Ramsdell, Eric Balles
Babcock Power, Inc.

Bio-medical imaging

Vivian Ortiz

Danielle Rand

Yanan Liu

Prof. Chris Laperle, Ph.D., *Providence College*

Milan Tatiček, *Czech Technical University*

Eva Sebronova, *Czech Technical University*

Barbora Kankova, *Czech Technical University*

Prof. Gerald Diebold, Ph.D, *Dept. of Chemistry, Brown University*

Prof. Zoltan Derdak, M.D.,

Prof. Jack R. Wands, M.D., *Liver Research Center, Brown Medical School, RI Hospital*



Funding

Department of Energy, BES

National Science Foundation

US Army Medical Research and Materiel Command

The Charles Stark Draper Laboratory, Inc.

Brown University Seed Fund

APS Partner-User, 2011 - 2013